Journal of Molecular Structure 1044 (2013) 299–302

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Degree of conversion and microhardness of dental composite resin materials

D. Marovic [a,*], V. Panduric [a], Z. Tarle [a], M. Ristic [b], K. Sariri [c], N. Demoli [c], E. Klaric [a], B. Jankovic [a], K. Prskalo [a]

[a] Department of Endodontics and Restorative Dentistry, School of Dental Medicine, University of Zagreb, Gunduliceva 5, 10000 Zagreb, Croatia
[b] Division of Materials Chemistry, Institute Rudjer Boskovic, Bijenicka 54, Zagreb, Croatia
[c] Laboratory for Coherent Optics, Institute of Physics, Bijenicka 46, Croatia

HIGHLIGHTS

- Light cured dental composite materials are tested.
- Degree of conversion of resin monomers to polymer network is measured.
- Fourier transform infrared spectroscopy and microhardness are compared.
- Microhardness could not substitute Fourier transform infrared spectroscopy.

ARTICLE INFO

Article history:
Available online 8 November 2012

Keywords:
Composite resins
Fourier transform infrared spectroscopy
Degree of conversion

ABSTRACT

Dental composite resins (CRs) are commonly used materials for the replacement of hard dental tissues. Degree of conversion (DC) of CR measures the amount of the un-polymerized monomers in CR, which can cause adverse biological reactions and weakening of the mechanical properties. In the past, studies have determined the positive correlation of DC values determined by Fourier transform infrared spectroscopy (FT-IR) and microhardness (MH) values. The aim of this study was to establish whether MH can replace FTIR for the determination of DC of contemporary CR.

Two nano-hybrid CR: Tetric EvoCeram (TEC; Ivoclar Vivadent, Liechtenstein) and IPS Empress Direct (ED; Ivoclar Vivadent) and one submicron-hybrid CR – Charisma Opal (CO; Heraeus Kulzer, Germany) were tested. DC was determined by using FT-IR ($n = 10$) and Vickers MH ($n = 10$) was measured using Leitz Miniload 2 Microhardness Tester (Leitz, Germany). The data were analyzed using ANOVA and Tukey's post hoc test ($p < 0.05$).

CO was the highest polymerized material (62.20%) in comparison to TEC (58.85%) and ED (58.78%). Opposite, ED was significantly hardest material (24.49) when compared to CO (17.81) and TEC (20.05).

Since the CO was the material with the highest DC, but also with the lowest MH, it can be concluded that the DC of new CR formulations cannot be estimated through the MH data.

1. Introduction

Dental composite resins (CRs) are most commonly used materials for the replacement of lost hard dental tissues. The resin matrix in their composition gives them plasticity and good handling properties, whereas filler particles are mostly responsible for the hardness, strength and other mechanical properties needed for the longevity of the material in the demanding conditions found in the oral cavity [1]. The material is in the plastic phase and its hardening occurs due to the visible light initiated cross-linking of resin monomers into a three-dimensional polymer network [2].

A high degree of composite polymerization is essential for the optimal physical properties [3] and the biocompatibility [4]. The conversion of monomers to the polymer is never complete and amounts up to 75% [5]. At the beginning of light irradiation, photo-initiators are activated and turn into free-radicals. The collision of free-radical initiators activates the monomers, which, in turn, activate other monomers and form covalent bonds between carbon atoms and form long-chain polymers. The lengthening and the interaction of the polymer chains cause an increase in the viscosity and the rigidity of the composite paste. The bridges of covalent bonds link the chains and form a cross-linked network. Within a rapidly stiffening structure, certain unreacted monomers remain trapped [6]. Residual unconverted methacrylate groups which may reside in lower parts of poorly polymerized composite fillings present not only cytotoxic and genotoxic risks [7–9], but

* Corresponding author. Tel.: +385 1 4899 203; fax: +385 1 4802 159.
E-mail address: marovic@sfzg.hr (D. Marovic).

0022-2860/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molstruc.2012.10.062

also their solubility might cause the formation of voids and the occurrence of secondary caries [7,10]. Therefore, the degree of conversion (DC) is the property which is often tested *in vitro*.

For the determination of the DC of dental CR, Fourier transform infrared spectroscopy (FT-IR) [2,11–14] and microhardness (MH) [3,15–17] are often used. Besides, other methods, such as Raman spectroscopy [11,14,18,19], differential scanning calorimetry [20], differential thermal analysis [14] and high performance liquid chromatography [21] are also used in dental research, but FT-IR remains the most often used technique. Infrared spectroscopy is used to determine the DC by the proportion of the remaining concentration of the aliphatic C=C double bonds in a cured composite sample relative to the total number of C=C bonds in the uncured material [22]. For dental CR based on methacrylates, which still represent the majority of CR, mid- (MIR) or near-infrared regions (NIR) can be used. In MIR, the intensity or area of the methacrylate stretch band at 1638 cm^{-1} is measured, which is correlated to the internal reference peak, whose intensity remains unaltered during polymerization process. This is the internal standard for normalization, which does not require measuring of the sample thickness [22]. Generally, composites based on methacrylates present aromatic bands at 1537 [23] 1583, 1608 [12] and 4623 cm^{-1} which can be used as internal standards [22]. In NIR, there are two aliphatic bands that can be used, at 6165 cm^{-1} (overtone = CH_2) and at 4743 cm^{-1} (=C—H), but the latter is not recommended due to the instability of the adjacent peaks [18]. The peak at the 6165 cm^{-1} does not require the internal standard and gives bulk polymer conversion data on sample geometry, unlike the measurements in MIR, which need extremely thin samples for measurement [18].

Another property of CR that may be important to consider is hardness. Hardness of composite materials is a property that enables it to resist plastic deformation, penetration, indentation and scratching. The microhardness of dental composite materials is usually used to predict their abrasion resistance if used as restorations in functional areas [24,25]. A positive correlation of volume fraction of filler and the Knoop hardness was found [26], as well as between mass fraction of fillers and Vickers microhardness [27,28]. Regarding the size of the fillers, it was found that composites containing nanofillers exhibit higher microhardness values than conventional composites due to more intimate contact of nanofillers with resin matrix than microfillers [28].

In past, many studies have determined the positive correlation of DC values determined by MH and FT-IR measurements [15,29], but there are also contrary reports [30,31]. The co-dependence of DC and microhardness is long known [29,32] and it was often used to indirectly assess the composites' depth of cure, which was defined as the deepest hardness value found equivalent to that at 0.5 mm depth [33]. Another method employed the difference in microhardness between the upper and lower surfaces of cured composite samples [34–36]. However, no correlation was found between DC and surface hardness [30,31]. It was observed that opaque materials and materials with high filler load, which exhibit stronger light scattering, consequently had lower DC and lower microhardness. Conversely, translucent shades were not influenced and they exhibited high DC and microhardness [37].

The aim of the study was to measure the DC and MH of contemporary CR and to establish whether MH values can be used instead of FTIR for determination of DC.

2. Experimental

2.1. Materials

Two nano-hybrid CR: Tetric EvoCeram (TEC; Ivoclar Vivadent, Liechtenstein) and IPS Empress Direct (ED; Ivoclar Vivadent) and one submicron-hybrid CR – Charisma Opal (CO; Heraeus Kulzer, Germany). Their composition, as stated by the manufacturers, is given in Table 1.

2.2. Methods

For FT-IR measurements ($n = 10$), a half of a rice grain amount of each CR was placed between two Mylar sheets and pressed under 10^7 Pa (1 cm in diameter, 0.1 mm thickness). The samples were polymerized using a Bluephase G2 LED polymerization device (Ivoclar Vivadent) in high power polymerization mode (1200 mW/cm^2) for 30 s. The uncured samples were pressed into KBr pellets ($d = 1$ cm) using spectroscopically pure KBr (Merck, Germany) with a Carver press. DC of polymerized samples was determined by Fourier transform spectrometer Mo. 2000 (Perkin Elmer, UK). Recording and processing of absorption spectra of composite specimens were carried out with Spectrum v5.3.1 software (Perkin Elmer, UK). Spectra of paired un-polymerized and polymerized composite specimens were recorded in a transmission mode at room temperature, corrected by subtracting the background and then converted into the absorbance mode (Fig. 1.). A total of 22 scans per sample were measured at a resolution of 4 cm^{-1}. DC (%) was calculated from the equivalent aliphatic (1638 cm^{-1})/aromatic (1608 cm^{-1}) molar ratios of cured (C) and uncured (U) samples according to the following expression [12]: $DC = (1 - C/U) \times 100$ (%).

MH samples ($n = 10$) were placed between two Mylar films and pressed between two steel plates to 0.85 mm thickness. Vickers MH was measured using Leitz Miniload 2 Microhardness Tester (Leitz, Germany) with the load of 5 or 10 g, 3 measurements for each load per sample. The Vickers microhardness was calculated according to the formula: $HV = 1.854\,P/d^2$, where P is the applied load in kg and d is the indentation in mm.

The data of DC and MH are expressed as means and standard deviations, and were analyzed using ANOVA and Tukey's post hoc test ($p < 0.05$). For the correlation of the DC and MH for each material, Pearson Correlation was used ($p < 0.05$).

3. Results

Fig. 1. shows the infrared spectra of tested composite materials in the region 1670–1580 cm^{-1}. Bands at ~1638 cm^{-1} represent the

Table 1
The composition of tested materials according to the manufacturers data. Bis-GMA: bisphenol A-glycidyl methacrylate; UDMA: urethane dimethacrylate; Bis-EMA: Bisphenol A polyethylene glycol diether dimethacrylate; TCDMMA – Tricyclodocandimethanoldimethacrylat, YT3 – ytterbium trifluoride; PFP – prepolymerized filler particles.

Material	Resin (vol.%)	Filler (vol.%)	Manufacturer	Shade, batch and expiration date
Tetric EvoCeram (TEC)	45–47% Bis-GMA, UDMA, Bis-EMA	53–55% Barium glass, YT3, mixed oxide, PFP (550 μm)	Ivoclar Vivadent, Schaan, Liechtenstein	A3; LOT N36895; Exp. 2014-05
IPS Empress Direct (ED)	41–48% UDMA, TCDMMA, Bis-GMA	52–59% Barium glass, YT3, mixed oxide, silicon dioxide and copolymer (40–3000 μm)	Ivoclar Vivadent, Schaan, Liechtenstein	A3 enamel; LOT N32078; Exp. 2014-03
Charisma Opal (CO)	42% Bis-GMA based matrix	58% Barium aluminium glass (0.02–2 μm) and highly dispersive silica (0.02–0.07 μm)	Heraeus Kulzer GmbH, Hanau, Germany	A3; LOT 010026; Exp. 2013–12